Communication

Sustainable Exploitation of Coffee Silverskin in Water Remediation

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Abstract: Coffee silverskin (CS), the main solid waste produced from the coffee industry, has efficiently been used as adsorbent material to remove potential toxic metals (PTMs). In order to assess its suitability in water remediation, kinetic adsorption experiments of Cu^{2+}, Zn^{2+}, and Ni^{2+} ions from wastewater were carried out and the adsorption performance of the waste material was compared with that of another well-known waste from coffee industry, spent coffee grounds (SCG). By using CS as sorbent material, ion removal follows the order $Cu^{2+} > Zn^{2+} > Ni^{2+}$ with the adsorption equilibrium occurring after about 20 min. The adsorption efficiency of Ni^{2+} ions is the same for both investigated materials, while Cu^{2+} and Zn^{2+} ions are removed to a lesser extent by using CS. Equilibrium-adsorption data were analyzed using two different isotherm models (Langmuir and Freundlich), demonstrating that monolayer-type adsorption occurs on both CS and SCG surfaces. The overall results support the use of coffee silverskin as a new inexpensive adsorbent material for PTMs from wastewater.

Keywords: potential toxic metals; coffee waste; coffee silverskin; spent coffee grounds; metal adsorption; remediation; Langmuir and Freundlich isotherm models; wastewater

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1. Introduction

In the past few years, in the framework of environmental sustainability research, numerous attempts on the reuse and valorization of coffee byproducts and coffee wastewater have been developed [1].

Coffee is the most important food commodity worldwide, being the second-most traded product after oil [2]. Because of this extended market, the coffee industry produces huge volumes of waste. In fact, each stage of the coffee production process (i.e., coffee-cherries processing, dried-beans milling, green-coffee-beans roasting), as well as coffee consumption, each year produces a large volume of biowaste, which contributes to environmental pollution [3]. Among this biowaste, residues with coffee silverskin (CS) and spent coffee grounds (SCG) are the most significantly produced. Since sustainability development has to be prioritized, research devoted to valorizing and reusing this kind of waste should be strongly encouraged in a strategy for the treatment of end-of-life materials [4].

CS is a thin integument of the outer layer of green coffee beans that comes off during the roasting process [5]. Moreover, it is generally produced in high volumes, takes fire very easily, and its disposal requires the use of energy for the necessary compaction process.

SCG are also a well-known residual material obtained from instant-coffee preparation or coffee brewing. SCG are a residue obtained during the treatment of raw coffee powder with hot

water or steam for instant-coffee preparation, characterized by fine particle size, high humidity, organic load, and acidity [6]. In order to reduce waste-disposal costs and avoid environmental pollution, coffee companies focus on possible alternative uses of SCG. Due to their composition, SCG possess functional properties, such as water-holding capacity, oil-holding capacity, emulsifing activity, and antioxidant potential, which make the material suitable for manifold applications (e.g., adsorbers, fillers, and additives for polymer composites, supplements in animal feed, soil fertilizers, etc.) [3,7]. Moreover, the suitability of spent coffee grounds as adsorbent for the removal of metal ions from aqueous solutions has been largely explored [6], whereas CS has not received, so far, the same attention. Currently, CS has no commercial value and is used only as fuel and soil fertilizer. Recently, some attempts were made to reuse it in different fields, for example, as a source of some bioactive compounds [7–9]. To this regard, the presence of undesirable products, such as ochratoxin, classified as a possible human carcinogen by the International Agency for Research on Cancer (IARC), strongly limits its use for food, cosmetic, and pharmaceutical purposes [10]. Therefore, alternative applications are desirable. As far as we know, the only example of its possible use was reported by Lavecchia et al., who magnetically modified the CS by contact with an aqueous ferrofluid containing magnetite nanoparticles in order to obtain a magnetic material adsorbent for the removal of xenobiotics from wastewater [11].

Potential toxic metals (PTMs) are commonly distributed in the environment, and their pollution sources stem from numerous industrial activities. Among these, zinc, nickel, and copper are essential elements for life and are micronutrients in trace amounts [12]; however, their untreated and uncontrolled discharge is toxic to ecosystems [13,14]. This toxicity affects humans causing several diseases (e.g., Wilson, Alzheimer's) and gastrointestinal problems [15,16]. Moreover, recent studies reported their negative effect on brain, liver, and carcinogenic diseases [17–20]. Therefore, the removal of Zn^{2+}, Cu^{2+}, and Ni^{2+} ions from wastewater streams is an important research task.

Despite various processes of PTMs elimination that are currently adopted (precipitation, electrocoagulation, membrane cementing or separation, solvent extraction, ion-resin exchange), adsorption is a cost-effective operation for the removal of potential toxic metals from diluted wastewater. Generally, commercially available zeolites or activated carbons are used as adsorbent materials [21]; however, owing to environmental sustainability problems, recent research has been oriented toward inexpensive and sustainable vegetable waste such as that deriving from tea [22], coffee [23], orange [24], and oil [25].

The present study aims to investigate the adsorption potential of selected metal ions (Zn^{2+}, Cu^{2+}, and Ni^{2+}) using the coffee silverskin coming from a local coffee roaster (Caffè Mauro S.p.A). Moreover, the adsorption properties of CS were compared with those of SCG, previously studied for removing metal ions from wastewater.

Thus, this contribution is focused on: (i) exploring the suitability of coffee silverskin for the removal of Zn^{2+}, Cu^{2+}, and Ni^{2+} ions from aqueous solutions by studying the retention profile of the latter under different analytical parameters (contact time, analyte concentration, pH); (ii) comparison of the adsorption properties of CS and SCG; and (iii) predicting the kinetic and isotherm models of metal-ion uptake.

2. Materials and Methods

CS and SCG were obtained from a local coffee roaster (Caffè Mauro S.p.A). All chemicals were purchased from CARLO ERBA and used without further purification. The metal sources used were nickel nitrate hexahydrate (99.9% purity), copper nitrate hemi (pentahydrate) (99.9% purity), and zinc nitrate hexahydrate (98.0% purity).

In order to remove impurities, CS and SCG were washed several times with hot water until the washing solution was colorless. Solids were then rinsed and oven-dried at 80 °C for 24 h. Finally, CS and SCG were ground, sieved to <100 μm, dried again at 150 °C for 24 h, and stored at room temperature until use, as similarly reported elsewhere [26].

Different batch tests were carried out to remove metal ions by single, binary, or ternary aqueous solutions.

The amount of solids used for all experiments was 0.12 g and the volume of aqueous solution was 20 mL, with a metal concentration ranging between 20 and 100 ppm, as previously reported [27].

After contact with metal solutions for a fixed time, the concentrations of metal ions in the filtered suspensions were determined using the ICP-OES instrument (Perkin-Elmer Optima 800, Waltham, MA, USA). Each of the experiments was carried out three times and the average value, having a deviation standard lower than 3%, was considered.

Solution volume was kept constant and adsorption efficiency was evaluated as follows:

$$\text{Adsorption \%} = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where C_0 (mg/L) is the initial concentration in aqueous solution, and C_t (mg/L) is the concentration at time t.

In order to investigate the morphological features and elemental compositions of adsorbent materials, characterization with the SEM-EDX technique was carried out on a Phenom Pro-X scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX). EDX analysis was used in order to evaluate the content and the dispersion of metals, acquiring, for all samples, at least 20 points for 3 different magnifications.

X-ray spectra were recorded with a Bruker D2 Phaser, using Cu Kα radiation at 30 kV and 20 mA. The peaks attribution was made according to the more known databases. Diffraction angles 2θ were varied between 10° and 80° in steps of 0.02° and a count time of 5 s per step [28,29].

The effects of pH on the adsorption of PTMs were examined to find the adsorption mechanism. The pH value was measured using combined glass electrodes (inoLab pH/Cond 720, WTW, Weilheim Germany). The concentration of metal ions in solutions was in the range 20–200 μM, with a pH value equal to 4.0.

The Langmuir (valid for monolayer sorption onto a surface with a finite number of identical sites and uniform adsorption energies) and Freundlich (applied to ions adsorption on heterogeneous surfaces) isotherm models were applied to study the adsorption behavior and to determine metal-adsorption capacity on CS and SCG.

The Langmuir isotherm is given by Equation (2):

$$q_e = \frac{q_{max}\, b\, C_e}{1 + b\, C_e} \tag{2}$$

where q_{max} is the amount of adsorption corresponding to the monolayer coverage, b is the Langmuir constant that is related to the energy of adsorption, and C_e is the equilibrium liquid-phase concentration. Equation (2) can be linearized to determine Langmuir parameters q_{max} and b.

$$\frac{1}{q_e} = \frac{1}{q_{max}\, b} \frac{1}{C_e} + \frac{1}{q_{max}} \tag{3}$$

The Freundlich equation allows calculating the parameters included in Equation (4) or, better, in linearized Equation (5):

$$q_e = K_f\, C_e{}^n \tag{4}$$

$$ln\, q_e = ln\, K_f + n\, ln\, C_e \tag{5}$$

where K_f (mg/g) is related to adsorption affinity, and $1/n$ is the heterogeneity factor related to the intensity of the adsorption.

Batch experiments on the adsorption of binary and ternary aqueous metal cation species in mixtures were carried out using the same initial total molar amount of cations.

3. Results and Discussion

3.1. Adsorption of Single Metals

The pH of the solution is a significant factor affecting the adsorption of metal ions since competitive adsorption between hydrogen/metal ions occurs. The investigated metal ions were present as Me^{2+}-deriving species (Cu^{2+}, Zn^{2+}, Ni^{2+}) forming, in water, coordinated aqueous complexes. Only at high pH values could hydroxyl species $Me(OH)_3^-$ and $Me(OH)_4^{2-}$ be detected. Preliminary tests, carried out by varying the pH, indicate that in order to achieve the dominant species for all metals, aqueous Me^{2+} complexes, the solution's pH value should be maintained in the range 4–5. In this range, no hydroxide precipitation occurs, as previously observed [30–32].

The adsorption isotherm of both materials used, CS and SCG, is shown in Figure 1. It is possible to notice that for both adsorbents the achievement of adsorption equilibrium occurs after about 20 min. To this regard, the adsorption efficiency of Ni^{2+} ions is the same for both materials, with a value of around 50%, whereas the CS adsorbent exhibits great efficiency in removing Cu^{2+} ions. On the other hand, SCG show higher efficiency, with respect to CS, in removing both Cu^{2+} and Zn^{2+} ions. The comparison of adsorption efficiencies, relative to both SCG and CS, may be better understood on the basis of the following consideration.
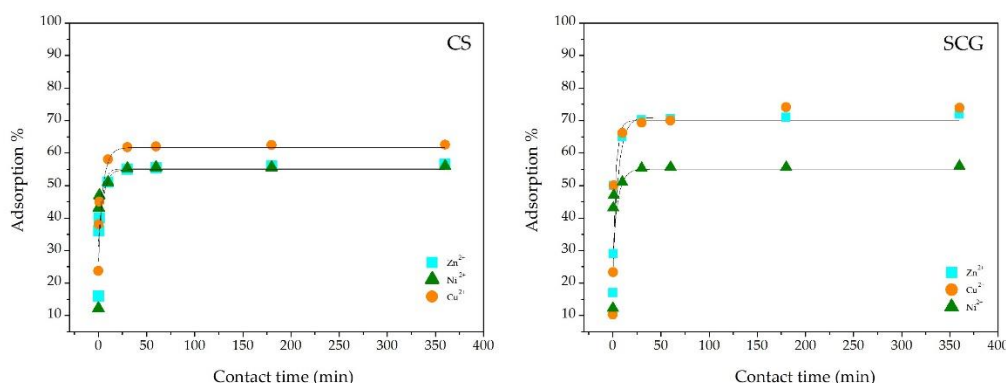

Figure 1. Contact time versus adsorption on coffee silverkin (CS) and spent coffee grounds (SCG) (C_0 = 100 ppm pH = 4 T = 25 °C).

The first stems from the different morphological features related to the external surface of both adsorbents. In principle, in fact, the presence of fissures and holes contributes to metal-ion diffusion through the adsorption surface. From the SEM micrographs shown in Figure 2, it is possible to infer the relevant differences in the CS and SCG morphological surface. SCG exhibit three-dimensional morphology formed by agglomerated grains, having dimensions of about ten microns, whereas CS shows a lamellar structure typical of vegetable teguments with a high surface area, preferentially ordered in two dimensions. Therefore, the bidimensionality of CS can contribute minor adsorption efficiency in comparison to that of SCG.

Another aspect that affects the observed adsorption difference can derive from the different amounts of lignocellulosic components in both structures (Figure 3). In principle, the adsorption ability of materials can be ascribed to favorable electrostatic interactions between positively charged metal ions and the opposite charge of the adsorbing surface. It is worth to underline that lignocellulosic biomasses are characterized by negatively charged surface sites, including hydroxyl and carboxyl groups as well as etheric oxygen atoms [33]. These groups belong to those generally called hard bases in the well-known hard and soft acid-bases theory [34,35]. Therefore, the higher content of lignocellulosic components in the SCG with respect to the CS contributes to explaining the higher adsorption efficiency of the former.
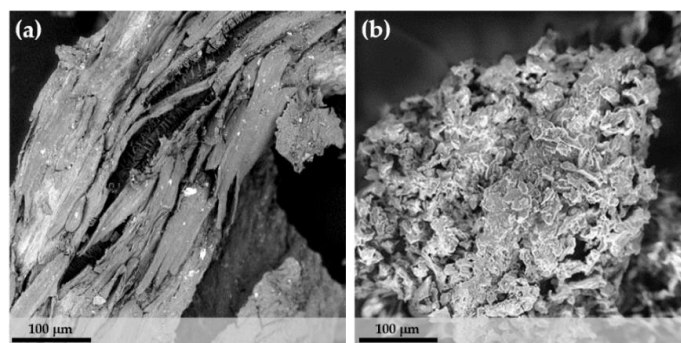
Figure 2. Scanning elecron microscope (SEM) micrographs of (**a**) CS and (**b**) SCG.
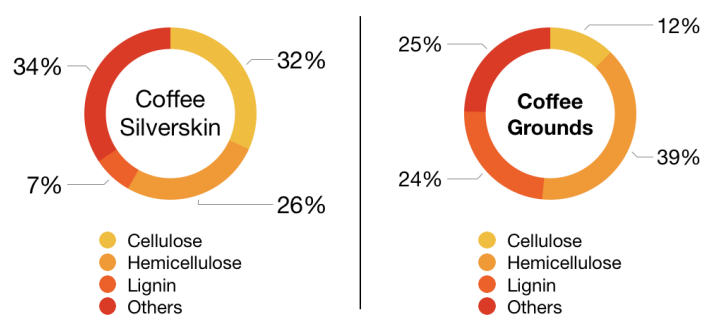

Figure 3. Compound composition of CS and SCG.

It is worth to emphasize that the investigated adsorbing materials were not affected by any contact with metal-ion solutions (Figure 4): the morphologies of CS and SCG were preserved and the mapping of metal ions confirmed the uniform distribution on materials recovered after the batch tests. The retention of metals by CS was also confirmed by X-Ray analysis on the CS recovered after batch adsorption. In Figure 5, it is possible to notice the deposition of nitrate salt precipitated on the adsorbing surface and peaks corresponding to Zn^{2+} species. Similar patterns were also recorded in other metal experiments (not shown). The precipitation of potassium nitrate is due to the leaching of potassium from the CS in the stirred conditions of the experiments. The mineral composition of the CS in fact mainly consists of potassium 5%w/w per 100 g of CS, determined by EDX analysis.
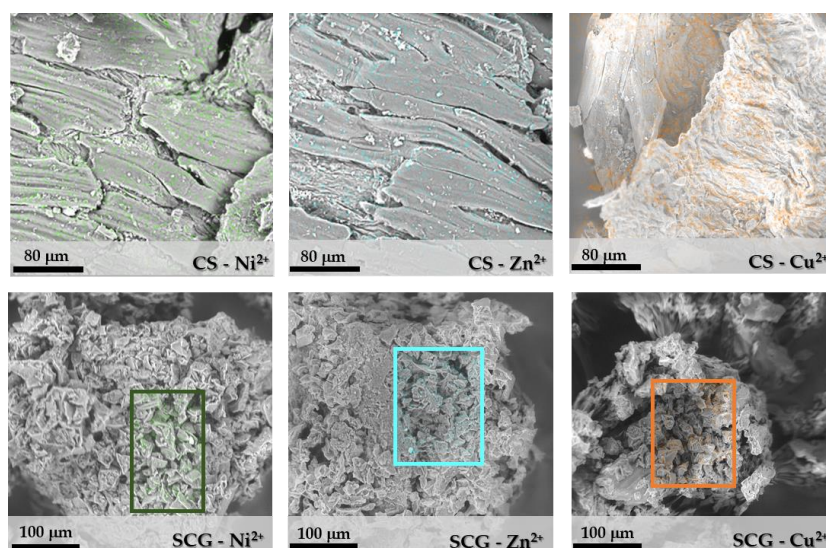

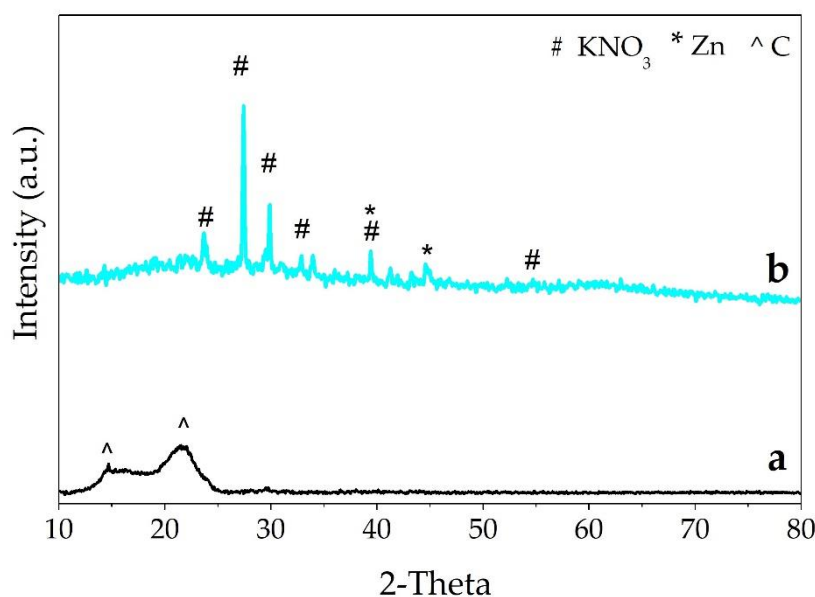**Figure 4.** SEM micrographs and energy-dispersive X-ray (EDX) maps of CS and SCG.

Figure 5. X-ray spectra of (**a**) CS as made and (**b**) CS after Zn^{2+} ion removal.

3.2. Isotherm-Model Application

Adsorption data relative to our systems were fitted by applying the Langmuir equation, and the results are reported in Table 1. Fitting was excellent for all metal-adsorbent systems considered (Figure 6) and the correlation coefficients of the linear regression (r^2) were found to be higher than 0.986 (Table 1).

Table 1. Langmuir and Freundlich isotherm parameters for Cu^{2+}, Zn^{2+}, and Ni^{2+} ions onto CS and SGC using a single-component solution.

PTM	Coffee Silverskin						Spent Coffee Grounds					
	Langmuir			Freundlich			Langmuir			Freundlich		
	q_{max}	b	r^2	K_f	n	r^2	q_{max}	b	r^2	K_f	n	r^2
Cu^{2+}	9.58	2.60	0.996	7.06	2.06	0.947	10.00	3.05	0.986	8.63	2.06	0.903
Ni^{2+}	1.43	15.05	0.994	1.30	13.00	0.827	1.67	20.22	0.999	1.58	13.00	0.981
Zn^{2+}	15.17	0.62	0.989	5.69	1.37	0.987	8.23	4.45	0.991	6.69	1.37	0.990

The maximum adsorption amounts on CS, fitted and obtained by the Langmuir model, were 15.17, 9.58, and 1.43 mg/g, respectively, for Cu^{2+}, Zn^{2+}, and Ni^{2+} ions. Therefore, the adsorption affinity of CS gives the sequence $Cu^{2+} > Zn^{2+} > Ni^{2+}$. A similar trend was observed for SCG.

From Langmuir isotherm coefficients, it is possible to also define dimensionless parameter R_L:

$$R_L = \frac{1}{(1 + bC_0)} \tag{6}$$

This can be considered a separation factor that can determine the type of isotherm [36].

Values of R_L denote if the type of the Langmuir isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$); in all our cases, values of R_L ranged between 0 and 1.

On the other hand, by applying the Freundlich isotherm models, adsorption affinity K_f values, relative to Cu^{2+}, Zn^{2+}, and Ni^{2+} ions on CS, were 7.06, 5.69, 1.30, respectively, indicating that Cu^{2+} and Zn^{2+} are preferably adsorbed. The n value indicates the degree of nonlinearity between solution concentrations and adsorption according to the following considerations: if $n = 1$, adsorption is linear;

if $n < 1$, adsorption implies a chemical process; if $n > 1$, adsorption stems from a physical process. The n values on using the Freundlich equation for Cu^{2+} and Zn^{2+} adsorption, both on the CS and on the SCG, are lower than 3 (Table 1). The value of $n > 1$ is very common and it is generally ascribed to dispersed surface sites or to any factor that may generate a decrease in adsorbent–adsorbate interaction. Generally, the increase of surface density and of n values, within the range of 1–10, means that adsorption was good [37]. In the present study, with respect to Cu^{2+} and Zn^{2+} ion adsorption, since n lies between 1 and 10, it is possible to infer that the adsorption of metal ions onto CS and SCG is essentially physical. For nickel ions, the n value, greater than 10, indicates minor mobility and a higher retention of metals in the solid phase [38].
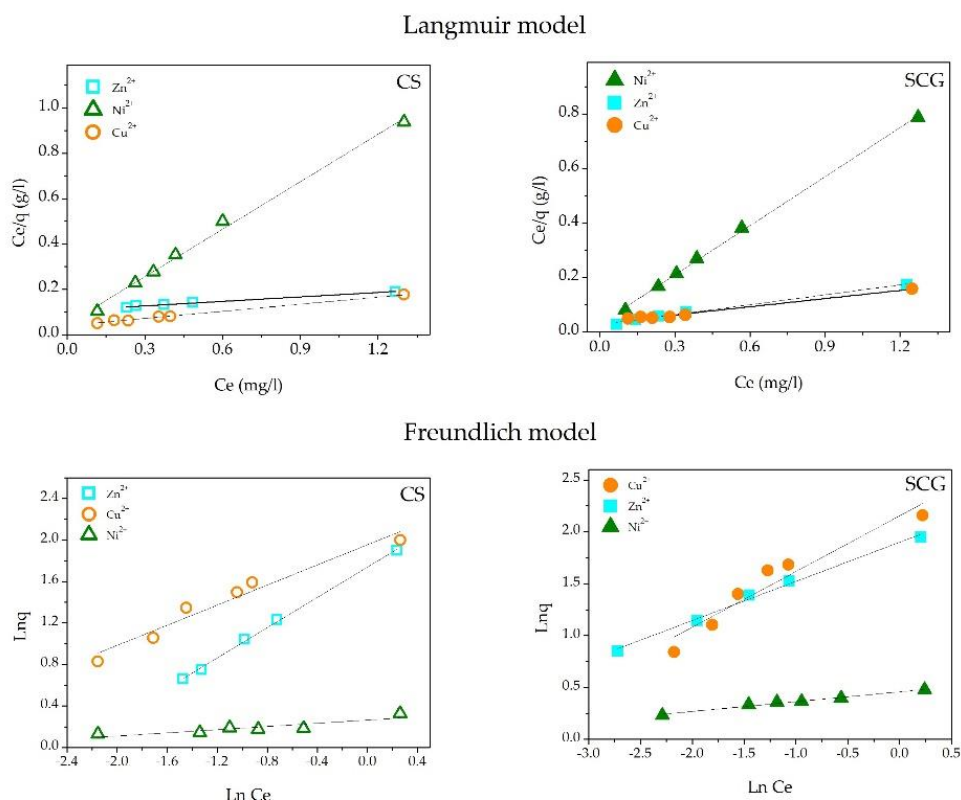

Figure 6. Langmuir and Freundlich isotherms for adsorption of metal ions on CS and SCG.

However, the results demonstrate that the fitting for all adsorbing materials is more suitable with the Langmuir model ($r^2 = 0.986$–0.999) for PTM adsorption than with the Freundlich one ($r^2 = 0.827$–0.987), so the adsorption characteristics were mainly of monolayer type.

3.3. Comparison of Metal Adsorption in Competitive Systems

In order to evaluate the affinity of metal ions towards the CS material, we also performed batch-experiment adsorption of binary and ternary aqueous metal cation species in mixtures Cu^{2+}/Zn^{2+}, Cu^{2+}/Ni^{2+}, Zn^{2+}/Ni^{2+} and $Cu^{2+}/Zn^{2+}/Ni^{2+}$ using the same initial total molar amount of cations.

Figure 7 shows the experimental data for binary and ternary mixtures and allows comparing the relative adsorption results with those obtained with separately using single metals.

In principle, in multicomponent system solutions, ions exhibit competitive adsorption. Therefore, the amount of cations adsorbed from binary solutions is lower than that obtained by using a single metal solution, and this is in agreement with other reports [30,39].

In particular, results suggest that the adsorption of metals on CS in a multicomponent system is, for all investigated metals, about 10%–15% lower than that detected in a single-component system.
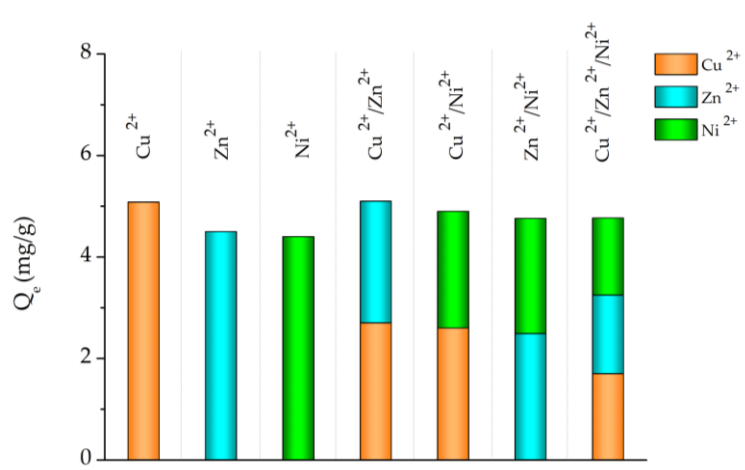
Figure 7. Single and competitive adsorption of Cu^{2+}, Zn^{2+}, and Ni^{2+} on CS: amount of metal ions adsorbed on CS.

However, total adsorption was higher than that observed in using a single component, in agreement with already observed results relative to other adsorbents [40,41]. The affinity order towards metals exploited by the CS material, both in the binary and ternary system, is the same as that found in the single one (Cu^{2+} > Zn^{2+} > Ni^{2+}).

The affinity and adsorption capacity of different metals could suggest a correlation between different metal parameters (e.g., electronegativity, coordination-complex radius, and stability constants of the associated metal hydroxide or solvated species) [42]. Electronegativity is regarded as a contributing parameter to metal-ion uptake. In fact, when metal cations are adsorbed on a negatively charged surface, the attraction of a negative charge plays a significant role in the adsorption process. However, this is not a general rule, as verified by different works on adsorption processes [9]. In principle, adsorption of metal cations on hard-containing surface groups depends on an interplay of factors belonging to both ions and surface. Indeed Ni^{2+}, Cu^{2+}, and Zn^{2+} have d^8, d^9, and d^{10} external electronic structure, respectively, and the observed trend towards their relative adsorption mainly depends on the stability of the aqueous coordinated complexes. All of them form octahedral $Me(OH_2)_6^{2+}$ complexes, and no information on their stability may be obtained from the literature. Furthermore, all three cations are considered on the borderline of the hard and soft acid and base classification [34,35].

4. Sustainability Considerations/Conclusions

Global coffee production has been extending to include a large industrial system, with a total coffee consumption of 157,858 in thousand 60 kg bags during the 2016/2017 period [42].

Among the huge volume of coffee waste as a result of the coffee production and consumption process, CS is generally considered the most significantly produced and, at the same time, difficult to manage. Indeed, CS represents not only solid waste that contributes to environmental pollution, but it also has high impact on the economy of coffee-roaster companies. In fact, the storage of CS before its disposal in compost or landfill needs specific machinery for compaction and relative high-energy consumption. Furthermore, its biomass releases both CO_2 and methane in landfills, with consequent environmental impact. Basically, the alternative to landfills is to bury or burn CS waste, with the unavoidable production of greenhouse gasses. According to the United States Environmental Protection Agency (EPA) [43], burning garbage constituted by biomass releases more carbon dioxide than burning coal. It is therefore clear that alternative solutions should be considered. Although a 'zero-waste' industry is not easily achievable in the near future, research must strive to be policy-aimed to achieve sustainable results in the reuse of byproduct materials [44].

The coffee waste used in this study derived from the roasting of green coffee beans. In order to perform the adsorption of potential toxic metals like Cu^{2+}, Zn^{2+}, and Ni^{2+} ions, no chemical modification or further treatment was used to obtain the adsorbing materials. This aspect is to be emphasized, since it is also necessary to ensure that waste treatment does not create any extra problems on the environment that could eventually undermine the beneficial effects of utilizing waste products such as CS or SCG [45].

Furthermore, CO_2 emissions should decrease due to the reduced use of incinerators for these organic wastes. Meanwhile, recovery of natural resources can be simultaneously achieved from the viewpoint of waste management.

Accordingly, the results of this preliminary laboratory work provide a possible sustainable route to recover inexpensive biological waste for its use as adsorbent of PTMs from wastewater. Further works will be devoted to identifying the regeneration methods of coffee silverskin, the recovery of the adsorbate, and the subsequent regeneration and reuse of the adsorbent material. Finally, quantitative consideration of sustainability (Life-Cycle Assessment, LCA analysis) on the applicability of CS and SCG in water remediation should be carried out in order to validate the entire process from an economical and environmental point of view.

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